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(54) **Process for preparing and processing a resin composition.**

(57) Resin compositions comprising two resins A and B, wherein resin A consists of the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol and a monovalent carboxylic acid and resin B consists of a carboxylic acid modified fatty acid ester of a polyvalent alcohol.
The resins compositions are suitable for linoleum manufacture.

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PROCESS FOR PREPARING AND PROCESSING A RESIN COMPOSITION

The invention relates to a resin composition comprising a mixture of two resins which is suitable for the preparation of a surface-covering layer, and in particular for the preparation of linoleum. Though the invention is expressly not limited to this, in the following the invention will be elucidated on the basis of the preparation of linoleum.

In the process so far applied for the preparation of a resin composition for linoleum manufacture (the resin composition hereinafter to be referred to as linoleum cement; in the linoleum preparation it is also called Bedford cement, after the manner it is formed), use is made of one or more polyunsaturated oils, which are 'dried' by air oxidation. Drying oils are understood to mean esters of natural fatty acids with polyvalent alcohols, in particular glycerol or pentaerithrytol. During or after drying, these drying oils are mixed with a resin, in particular with colophonium, yielding the Bedford cement. This cement is mixed with fillers and pigments, following which the linoleum mix thus obtained is applied to a, mostly jute, substrate, usually with the aid of a twin roller mill. The product formed is cured at 60–80 °C for a number of weeks (see, e.g., Ullmann, Encyklopädie der technischen Chemie, Band 12 (1976), p. 24 ff. and Encycl. of Pol. Sci. and Techn. Vol. 1 (1964), p. 403 ff.).

The disadvantage of the process that has so far been customary for the preparation of linoleum is the long time required for curing of the product, while this time depends on the thickness of the linoleum layer. Furthermore, intensive manual inspection is required to determine whether the desired hardness has been reached.

Shortening of the drying time has been investigated before, but none of the possible solutions suggested has found wide application (Encycl. of Pol. Sci. and Techn. Vol. 1 (1964), pp. 103/4).

The invention described here provides a resin composition which is eminently suitable as linoleum cement, the time for the necessary curing of the linoleum being substantially shortened and the homogeneity of the material thus obtained being improved.

The resin composition according to the invention, comprising a mixture of two resins, hereinafter to be called A and B, is characterized in that resin A consists of the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol and a monovalent carboxylic acid, and in that resin B consists of a carboxylic acid-modified fatty acid ester of a polyvalent alcohol. The term 'carboxylic-acid-modified' in this context also covers the presence of carboxylic-anhydride groups instead of, or besides, carboxylic acid groups.

The linoleum curing method that has until now been customary is based on oxidative 'drying' of the double bonds still present in the oils applied, use being made of liquid driers (e.g. leaddecanate). When a resin composition according to the invention is applied, 'drying' takes place by crosslinking of the reactive groups already present in the product, eliminating the exclusive dependence in the manufacture on diffusion of oxygen from the air to and in the product. An additional advantage is that curing takes place much more uniformly throughout the material, which has a favourable effect on the product properties. Application of the resin composition according to the invention still allows air after-curing, which in some applications is desirable in view of the required ease of handling of product not yet fully cured during final processing.

Surprisingly, it has been found that when applying a resin composition according to the invention the curing time of the linoleum obtained in accordance with the invention can be reduced substantially in comparison with the application of Bedford cement according to the technique known since long.

Where linoleum hardness is controlled using the curing time in traditional processes, it has been found that the degree of hardening of a linoleum prepared in accordance with the invention can be controlled by the degree to which carboxylic acid groups are present in resin B.

Linoleum cement obtained according to the invention has a lower viscosity than cement obtained by the traditional method. As a result, mixing of fillers and pigments to obtain the linoleum mix can be greatly simplified.

One of the most important drying oils currently used for linoleum preparation is linseed oil, which is oxidized with atmospheric oxy-

gen to convert it into a solid, rubbery, elastic material called Linoxyn. Other oils, drying less rapidly, such as soy-bean oil, sunflower oil, or a tall oil fatty acid ester, are applied solely or in combination with linseed oil. Surprisingly, it has been found that in the preparation of a linoleum according to the invention not only linseed oil can be applied, but also said oils having a longer drying time, both separately and combined, without any great lengthening of the curing time taking place.

In the resin composition according to the invention a combination of two resins is applied, both resins being prepared on the basis of such a (modified) drying oil.

The drying oil in resin A is applied in epoxidized form, use being made in particular of an epoxide of soy-bean oil, linseed oil, sunflower oil and/or a tall oil fatty acid ester. The polyvalent alcohol used for esterification is preferably chosen from the group formed by glycerol, pentaerithrytol and trimethylolpropane. Mixtures of these or other polyvalent alcohols such as polyalkylene glycols may also be applied.

For the monovalent carboxylic acid in resin A use may be made of, for instance, benzoic acid, para-tertiary-butyl-benzoic acid, rosin, talloil fatty acid, stearic acid and/or mixtures of these. For the linoleum preparation preference is given in particular to rosin as monovalent acid, this with a view to retaining the properties characteristic of linoleum which originate from the rosin. Besides the monovalent carboxylic acid referred to, use may also be made of a combination with a polyvalent carboxyl acid, e.g. up to 10 mol % (relative to the total amount of carboxylic acid). Suitable carboxylic acids for this purpose are those with 4-54 C-atoms in the molecule. In particular, a di- or trimer fatty acid, or a mixture thereof, or acid terminated polyesters can be applied as polyvalent carboxylic acid.

The carboxylic acid-modified ester in resin B advantagously consists of the reaction product of an unsaturated fatty acid ester of a polyvalent alcohol and one or more ethylenically unsaturated mono- or polyvalent carboxylic acids or their anhydrides. As unsaturated fatty acid ester, a vegetable oil or a tall oil fatty acid ester can be started from, esterification having been effected in particular with a polyvalent alcohol from the group formed by glycerol, pentaerithrytol

and trimethylolpropane, while mixtures of these or other polyvalent alcohols can also be applied. In the context of this invention, suitable vegetable oils in particular are soy-bean oil, linseed oil, olive oil, safflower oil and/or rape seed oil.

The ethylenically unsaturated carboxylic acid, or its anhydride, used for the preparation of resin B, may contain one or more ethylenically unsaturated groups in the molecule. As monovalent carboxylic acid, use can preferably be made of acrylic acid, methacrylic acid, sorbic acid and/or crotonic acid. As polyvalent carboxylic acid, use can preferably be made of maleic acid and/or fumaric acid. Maleic anhydride is particularly suitable for the purpose, the so-called maleinated oils being easy to prepare and commercially available.

The carboxylic acid-modified ester in resin B may also consist of the reaction product of a hydroxy-functional fatty acid ester of a polyvalent alcohol and a polyvalent carboxylic acid. For this, in particular the esters can be applied that are derived from castor oil, hydroxystearic acid and/or hydroxypalmitic acid. The polyvalent alcohol used for esterification then is preferably chosen from the group formed by glycerol, pentaerithrytol and trimethylolpropane. Mixtures of these or other polyvalent alcohols can also be applied. The polyvalent carboxylic acid that is reacted with the above-mentioned hydroxy-functional fatty acid ester can by preference be taken from the group formed by phthalic acid, tetra- or hexahydrophthalic acid and trimellitic acid.

Besides the description of resin B given in the above, said resin may also consist of one or more acid-functional alkyd resins.

In the preparation according to the invention by preference first resin A is prepared by reacting the epoxidized ester with the monovalent carboxylic acid. This preparation takes place at a temperature of 100 to 250 °C and by preference of 150 to 200 °C, optionally in the presence of a catalyst. As catalyst, by preference the customary catalyst for the acid-epoxy reaction is applied, for instance triethylamine.

Preparation of the resin composition according to the invention is preferably effected by combining resin A with resin B at a temperature of 60 to 150 °C, and preferably at a temperature of 80 to 100 °C. For this, a catalyst of the same type as in the preparation of resin A can be used.

In the preparation of linoleum subsequently the fillers and other additives are added, everything being done exactly as is customary in present-day linoleum production.

Curing of a linoleum prepared according to the invention then takes place at a temperature of 50 to 95 °C in some hours or days, depending on the desired linoleum quality, which in its turn is determined by the component mix applied.

Since curing of the linoleum obtained according to the invention takes place by chemical crosslinking rather than by oxidative drying, as in the traditional method, it is now possible to replace the time-consuming, manual final inspection by a more instrumental setting of the drying conditions, which depend on the desired properties of the linoleum to be prepared, which in their turn are determined by the composition of the linoleum cement used.

Though the preceding mainly discussed the application of the resin composition according to the invention in the preparation of linoleum, the application of the resin composition obtained according to the invention is not restricted thereto.
Other systems using resin compositions, customarily in the form of so-called two components resins, to obtain a surface covering layer are also suitable for application of this resin composition. Among the applications that can be considered are roof coverings and the so-called 'Unterbodenschutz' in the automotive industry.

The invention will be elucidated with reference to the following non-restrictive example.

Example 1

Preparation of resin A1

A 3-l reaction vessel provided with a mechanical stirrer, thermometer and a vertical cooler is supplied with 60 parts by weight epoxidized linseed oil (Edenol B 316 of Henkel with an oxirane content of more than 8.5 %), 40 parts by weight rosin and 1 part by weight triisobutylamine. While nitrogen is being passed over it, the reaction mixture is heated to 180 °C. The contents of the reaction vessel are kept at this temperature until the acid number has decreased to 3 mg KOH/g. The product is subsequently cooled. The epoxyequivalentweight is 600.

Preparation of resin B1

In equipment similar to that used for resin A1, 878 parts by weight linseed oil are heated to 200 °C under nitrogen. Next, 294 parts by weight maleic anhydride are cautiously added, divided into portions over two hours. Care is taken that the temperature does not rise above 200 °C. After everything has been added, the temperature is gradually raised to 225 °C and maintained for 4 hours.

Preparation of the resin composition

The components obtained according to 1) and 2) are mixed in a ratio of 1 : 1. In line with the known linoleum technique, cork powder, chalk and pigments are added. The linoleum mix (mix 1) obtained is then cured in sheets at 80 °C during 3 hours. An elastic, tough linoleum material is obtained.

Example 2

Preparation of resin A2

In the way as described in Example 1 (resin A1), 79 parts by weight of epoxidized soja oil (Edenol D81, oxirane content above 6.0 %, ex Henkel), 18 parts by weight of p-tertiarybutylbenzoic acid, 1.6 parts by weight of dimerised fatty acid (Empol 1014, ex Unichema Chemie, 5 mol % 20 calculated on total carboxylic acid) and 1 part by weight of triisobutylamine were charged to a 3 l reaction vessel. The mixture was heated to 180 °C and kept at that temperature until the acid value was 1.4 mg KOH/g. The epoxy equivalent weight was 668.

Preparation of resin B2

In the way as described in Example 1 (resin B1), 67 parts by weight of Castor oil (hydroxyl-value 160-170 mg KOH/g) and 33 parts by weight of trimellitic anhydride were charged to a 3 l reaction vessel. The mixture was heated to 180 °C at which temperature the trimellitic anhydride dissolved and reacted.
The acid value of the product was 195 mg KOH/g.
(Theory: 195 mg KOH/g).

Example 3

Preparation of resin compositions

The compounds as prepared in examples 1 and 2 were mixed in the following proportions, together with cork powder, chalk and pigments, in line with the known linoleum techniques:

Mix 2: 2 parts of resin A1 and 5 parts of resin B2

Mix 3: 1 part of resin A2 and 1 part of resin B1

Mix 4: 2 parts of resin A2 and 5 parts of resin B2

The linoleum mixes were then cured in sheets at 80–120 °C during 1-4 hours.

Elastic, tough linoleum materials were obtained.

CLAIMS AE 3566

1. Resin composition comprising at least two resins, hereinafter referred to as A and B, characterized in that resin A consists of the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol and a monovalent carboxylic acid, while resin B consists of a carboxylic acid-modified fatty acid ester of a polyvalent alcohol.

2. Resin composition according to claim 1, characterized in that resin B consists of the reaction product of an unsaturated fatty acid ester of a polyvalent alcohol and one or more ethylenically unsaturated mono- or polyvalent carboxylic acids or their anhydrides.

3. Resin composition according to claim 1, characterized in that resin B consists of the reaction product of a hydroxy-functional fatty acid ester of a polyvalent alcohol and a polyvalent carboxylic acid or anhydride.

4. Resin composition according anyone of claims 1-2, characterized in that the fatty acid ester of resin A and resin B are selected from soya bean oil, linseed oil, sunflower oil, olive oil, safflower oil, rapeseed oil, and/or a tall oil fatty acid ester.

5. Resin composition according to any one of claims 1-4, characterized in that the polyvalent alcohol of resin A and resin B are selected from glycerol, pentaerithrytol, trimethylolpropane and/or a polyalkyleneglycol.

6. Resin composition according to any one of claims 1-5, characterized in that the monovalent carboxylic acid of resin A is selected from benzoic acid, para-tertiary-butyl-benzoic acid, talloil fatty acid, stearic acid and/or rosin.

7. Resin composition according to any one of claims 1-5, characterized in that the carboxylic acid of resin A is rosin.

8. Resin composition according to claim 2, characterized in that the ethylenically unsaturated carboxylic acid of resin B is selected from acrylic acid, methacrylic acid, sorbic acid, crotonic acid, fumaric acid and/or maleic acid and/or the anhydride thereof.

9. Resin composition according to claim 3, characterized in that the hydroxy-functional fatty acid ester is selected from castor oil and esters derived from hydroxystearic acid and/or hydroxypalmitinic

acid, and from glycerol, pentaerithrytol, trimethylolpropane and/or polyalylene glycol.

10. Resin composition according to any one of claims 3 and 9, characterized in that the polyvalent carboxylic acid or its anhydride in resin B is phthalic acid, tetra- or hexahydrophthalic acid and/or trimellitic acid and/or the respective anhydride.
11. Resin composition according to claim 1, characterized in that resin B consists of one or more acid-functional alkyd resins.
12. Process for the preparation of a resin composition according to any one of claims 1-11, characterized in that resin A and resin B are prepared, following which the resin composition is obtained by combining resin A and B at a temperature of 60-150 30 °C and preferably at 80-120 °C.
13. Object made wholly or partly using a resin composition according to any one of claims 1-11.
14. Surface-covering layer, in particular linoleum, prepared using a resin composition according to any one of claims 1-11.